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Dynamic Processes of Optically Induced Birefringence of Azo

Compounds in Amorphous Polymers below T_g

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Abstract

The growth and decay processes of the optically induced birefringence in an azobenzene functionalized polymer, DR19FPOZ (full name given in the text) and in another azobenzene guest/host polymer system have been studied. The temperature dependence of the birefringence signal is studied and possible mechanisms associated with the growth and decay segments of the signal are analyzed. Rate constants deduced from the optically induced birefringence signal are also investigated as a function of the laser excitation power and film thickness. The rate constants associated with the growth and decay processes and activation energies are obtained from the Arrhenius plots of the temperature dependent rate constants below the glass transition temperature of the polymer system..

INTRODUCTION

The photoinduced trans-cis isomerization of azobenzene and its derivatives have been widely studied in solution,[1] and in doped and functionalized glassy polymers.[2] In recent years, numerous studies have also been carried out in order to clarify the mechanism, in the hope of developing applications in the fields of electrooptical devices, polarization holographic grating and nonlinear optics.[3-5] This type of photoinduced isomerization process is of particular interest because the induced changes in molecular orientation can also be transferred to the surrounding molecules.[4,6] In addition, the induced birefringence and dichroism as a result of molecular reorientation could also be used to probe the local polymer environment in the vicinity of the azobenzene molecules.[2]

The photoinduced orientation of azobenzene derivatives begins with a trans-to-cis photoisomerization. When first dispersed in a polymer film, the orientational distribution of azo compound is isotropic. If the polymer film is then subjected to polarized light that could be absorbed by the azo compound, the molecules with a transition dipole having a non-vanishing component along the polarization vector direction of the excitation beam can be photoisomerized to the cis form. Through a thermal or photochemical process the cis form can also revert back to the trans form, although not necessarily to its original orientation. After several repetitive isomerization cycles, an excess azo molecules with transition dipole moments aligned perpendicular to the polarization vector direction of the excitation light could develop, because in this orientation the azobenzene molecules cannot interact with the excitation light and will not be converted back to their original isomeric form. As a result, the distribution of molecular orientation that was isotropic

before photoexcitation becomes anisotropic. This anisotropic distribution gives rise to birefringence and dichroism in the film.[3]

The time required to reach the maximum birefringence depends on several factors such as the size of the azobenzene molecules, the thickness of the film, and the wavelength of the excitation light and its intensity. Numerous studies of such effects on the dynamics of the photoinduced orientation of azobenzene functionalized polymer have recently been performed by Natansohn et al.[7] These authors have reported a two mode pattern in the growth and decay segments of the photoinduced birefringence signal.[8] However, detailed mechanisms with regard to the dynamic photoinduced birefringence signal have not been clarified. In addition, there are very little temperature dependent studies of the photoinduced birefringence signal been made. To clarify the mechanisms responsible for the dynamic birefringence signal, we have studied the laser intensity and temperature dependence of the photoinduced orientation process. In addition, we have also measured the effects by varing in film thickness. In this paper we present the results of these studies.

EXPERIMENT

Figure 1 shows the chemical structure of the Disperse Red19 (DR19) functionalized polyoxazolidone polymer (DR19FPOZ) which was used in the present study. DR19 was made in house using standardized procedure.[9] DR19FPOZ was also synthesized in house. The synthesis was performed according to the literature procedure.[10] To obtain the DR19FPOZ polymer, bis-phenol-A diglycidylether (3.4 mg, 0.1 mmol) and prepolymer (8.6 mg, 0.1 mmol) were dissolved in 10 mL of dioxane. The

synthesis of prepolymer containing the azobenzene chromophore was carried out by using the procedure described in ref. 10. The resulting solution was filtered through a 0.1 μm Teflon filter and was then spin-cast onto several clean glass substrates. The resulting films were dried under vacuum at room temperature to remove solvent. After the solvent was removed, the films were placed in an oven and heated to 120°C to initiate polymerization by keeping them at that temperature for at least 5 hours . In order to monitor the polymerization process, a film was prepared on a NaCl substrate under the same conditions as the other films described above. After the polymerization process was completed, the IR spectrum of the film prepared on the NaCl substrate was measured and found to be identical to that given in the literature.[9] Thus, the successful preparation of the DR19FP0Z polymer films was assured.

Figure 2 shows the setup for the measurement of photoinduced birefringence. The 488.0 nm line from an Ar^{+} laser was used as a pump (or writing) beam and a 632.8 nm line from a He:Ne laser was used as a probe (or reading) beam. The wavelength of the pump beam is in the absorption range of the DR10FP0Z polymer and the wavelength of the probe beam is outside of the absorption range. To carry out the experiment, a film sample was placed between a pair of crossed polarizers. The polarization vector of the pump beam was set at 45° with respect to the polarization vector of the probe beam to achieve the maximum signal. An electronically controlled shutter was used to turn on and off the pump beam and, when needed, a quarter wave plate was inserted into the optical path to remove the birefringence that had been photoinduced. The signal (i.e. the transmitted probe beam) was detected by using a photomultiplier tube. To investigate the temperature

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dependence of photoinduced birefringence, the film was placed in a computer-controlled sample oven which regulated the temperature to ± 0.1 °C.

Results and Discussion.

Photoinduced trans-cis isomerization in azobenzene is a well-known process. Azobenzene derivatives derivatives characterized by a N=N double bond usually display a low-intensity n-π^* band in the visible region and a high intensity π-π^* transition in the UV region. Due to an increase in the π orbital and a decrease in the π^* orbital energy level, the n-π^* and π-π^* bands in ortho- and para-aminoazobenzene molecules tend to move close together or even overlap.[1] This effect is especially enhanced when 4 and 4' position are substituted with electron donor and electron acceptor groups, the typical configuration of nonlinear optical (NLO) chromophores. Azobenzene derivatives capped with an electron donor and acceptor groups, such as disperse red 1 (DR1) and DR19FPOZ polymer considered here, have a transition dipole moment lying along the long π-conjugation direction. The N=N bond can be easily broken with light with frequency in the absorption band of the molecule. As a result of the light-molecule interaction, molecules having the π-conjugation direction parallel to the polarization vector of the laser beam are excited; they then undergo a trans to cis isomerization process by first going to the first excited state of the trans form (π^*) before relaxing to the ground-state cis form after first performing a rotation about the N-N bond. The cis form may also be converted back to the trans form by a photo or a thermal process. The photoisomerization from trans to cis or from cis to trans form is a fast process; it takes place in the sub-nano to

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picosecond time regime. The photoinduced isomerization rate depends on the laser excitation intensity and on the environment in which the azo moiety situates; however, the thermal induced relaxation of the cis isomer and the reorientation of both cis and trans isomers are slow and the rates these slow processes are not expected to depend on the intensity of the excitation laser due to the fact that the power used in the photo-excitation experiment is rather low.

In the guest/host system, azobenzene molecules with orientation parallel to the polarization vector of the excitation light are readily excited to the first excited state, followed by the breaking of the π bond of the N=N linkage.[11] Free rotation of the N-N bond can also readily occur in the first excited state and the trans isomer with orientation vertical to the polarization vector of the laser light can then easily be formed. In the azobenzene functionalized polymer, free rotation of the N-N bond in the first excited state following the breaking of the π bond cannot yield a cis isomer. However, because one end of the azo benzene is tethered to the polymer backbone, the trans isomer in another orientation cannot be easily formed. Nevertheless, the N atom in the `amine groups in the functionalized polymer in the first excited state, which initially has a sp^3 character before excitation, now assumes a sp^2 hybridization character and therefore possesses a geometric coplanar symmetry. As the excited molecule relaxes to the ground state, the N-atom in the amine group resumes again a sp^3 pyramidal structure; in this case the N atom can either move above or below the geometric plane. Thus, by a proper adjustment of the N atom position through orbital hybridation plus a rotation about the N-N bond of the nitro benzene group, and also in combination with the local segmental motion of the polymer chain, a trans isomer in another orientation can then be obtained. All of these concerted

motions are necessary steps to execute the cis to trans photoisomerization process of the azobenzene functionalized polymer to yield a trans form with the N=N bond oriented in a different direction. Even so, this complex cis to trans isomerization in the azobenzene functionalized polymer, if it occurs, is also expected to be fast (in the subnano to picosecond time range) as in the process electronic transitions are involved. The rate of this cis to trans photoisomerization is expected to depend on the laser power. The above suggests that with the help of light a conformational change for polymers in the glassy state can occur via photoisomerization, despite the fact that rotation of the chemical group about the N-N bond is hindered and the mobility of the polymer chain is rather restricted. A similar conclusion has also been reached in other polymer system below T_g [13]

Shown in Fig. 3 are representative growth and decay traces of the birefringence signals of disperse red 1 (DR1) in poly(methylmethacrylate) (PMMA) matrix (top) and of the DR19FPOZ polymer (bottom) at room temperature. At the beginning of the experiment, there is no signal transmitted through the analyzer that is vertical with respect to the first one which is placed in front of the sample. Before optical excitation, the orientational distribution of the azo compound is isotropic and there is no birefringence. As the polarized Ar^+ laser radiation at 488 nm is introduced (marked "A" in the figure) an anisotropic orientation distribution is created as a result of the accumulation of the cis isomers and trans isomers oriented in orientation differing from the original one and the signal is then transmitted due to the onset of optical birefringence. As the excitation light is turned off (marked "B" in the figure), the signal starts to decay because of the orientational relaxation back to equilibrium. In the guest/host system (top figure), the decay to the background signal level is rapid and a complicate recovery to the background

signal occurs in a short time. On the other hand, in the DR19FPOZ functionalized polymer (bottom figure), the signal does not relax back to equilibrium within the time of the experiment. To rapidly remove the remaining birefringence, one needs to introduce the circular polarized light. (marked "C" in the bottom figure). The circular polarized light effectively converts the cis isomer to trans form in all orientation. The transmitted signal, I, due to birefringence is proportional to $\sin^2\left(\dfrac{\pi d \Delta n}{\lambda}\right)$, where d and Δn are the thickness and birefringence of the film, respectively; λ is the wavelength of the probe beam (the He-Ne laser radiation at 632.8 nm). The dynamics of the transmitted signal is thus due entirely to the time dependence of Δn.

We have investigated the temperature dependence of the growth/decay birefringence signal. Shown in Fig. 4 are the signals obtained at several temperatures. The maximum level of the birefringence signal decreases rapidly as the temperature is increased near or above T_g.($\approx 100°$ C). Near or above T_g, the signal relaxes rather fast and it needs a different experimental technique to accurately resolve the rapid time dependence process for the system at high temperature. This will be a topic of our future work; in the present paper we focus on the dynamic process of the DR19FPOZ polymer below T_g.

The growth of the birefringence signal is not single exponential but it can be adequately fit to a bi-exponential function given by

$$I(t) = A(1 - e^{-k_a t}) + B(1 - e^{-k_b t}) \tag{1}$$

,as shown by the top figure of Fig. 5, where A and B are amplitudes associated with the processes having rate constant k_a and k_b, respectively. The decay of the signal after the removal of the excitation beam is also bi-exponential and can be fit to

$$I(t) = Ce^{-k_c t} + De^{-k_d t} + E \qquad (2)$$

(the bottom figure in Fig. 5), where C and D are amplitudes associated with the processes having rate constants k_c and k_d, respectively. E is the background intensity, which can be minimized to a vanishingly small number if circular polarized light is introduced to erase the residual birefringence, as mentioned above. Natasohn et al.[7] have also observed the bi-exponential kinetic process in azobenzene systems. Although these authors have not carried out a detailed analysis of the growth/decay curve, they have proposed a model to describe kinetics of the signal such as the ones illustrated in Figure 3. In their model, only trans isomers oriented with some specially designated orientational distribution with respect to the polarization vector of the probe beam are assumed to contribute to the signal. Molecules in the cis configuration are neglected as they are assumed to make no contribution to the birefringence signal. Although a simulation based on this model with a specially constructed set of parameters is able to reproduce the general features of the experimental results, their simulated results render the kinetic rate constants associated with the growth and decay curve to depend on the intensity (photon flux) of the writing beam. Their model clearly does not agree with the analysis presented above. Our experimental results also do not support the simlution result.

To start, we have examined the effect of the writing power on the signal growth and decay segments. The time dependence of each signal obtained with a different writing laser power is analyzed. Both the growth and decay segments obtained at each power lever appear to fit well to the bi-exponential functions given above. The results for the parameters A, B, k_a and k_b for three lowest writing laser power are given in Figure 6. One notes that k_a and k_b, the rate constants related to the growth segment, display no writing laser power dependence. However, the amplitude of the fast process (associated with k_a) shows an increase with increasing the writing laser intensity; on the other hand, the slow process (associated with k_b) shows a reverse intensity dependence. As mentioned above, in the azobenzene functionalized polymer, while the cis isomer can be readily induced by the Ar^+ laser beam, in contrast to the guest/host system, the isomerization of cis to trans form with different orientation from the original one cannot be easily take place. Thus, we believe that in the DR19FPOZ polymer, the orientation of the cis isomer contributes significantly to the growth of the birefringence signal. The fast process with an amplitude that increases with increasing writing laser intensity is probably associated with the production of the cis isomer. In the presence of the laser radiation, the cis isomer can be converted to a trans isomer with different orientations through the orbital hybridization of the N-atom of the amine group accompanied by local motion of polymer segments. The trans isomer in new orientation contributes to the birefringence signal, where the initial trans isomer to which the cis isomer can also be reverted back will not contribute to the birefringence signal. Thus in the DR19FPOZ polymer both cis and trans isomers contribute to the birefringence signal. K_a and k_b are rate constants arising from reorientational transitions among different trans and cis isomers. At room temperature we

find that the rate constants k_a is greater than that of k_b by a factor of about 10 and both do not depend on the laser intensity.

Shown in Figure 6 is the dependence of rate constants k_c and k_d on the writing laser intensity. No power dependence of k_c and k_d is found; neither do the amplitudes C and D depend on the laser power. This is expected because the writing Ar^+ laser is turned off when the decay segment is measured. Our results should be contrast with the conclusion of ref. 7 in which the writing laser intensity dependence of the time constants associated with the decay segment is asserted.

Temperature dependence data will provide an additional insight into the mechanisms involved in the growth / decay segments of the birefringence signal. Shown in Fig. 7 is the temperature dependence of k_a and k_b. It should be pointed out that due to the physical aging effect below Tg, relaxation rates are found to gradually decrease with time from the freshly prepared sample. The data presented in Fig. 7 are obtained after the films have been aged by about one month. Within the experimental uncertainty, both k_a and k_b show a similar activation energy of about 7.0 kcal/mol. The temperature dependence of the rate constants k_c and k_d associated with the decay segment is very interesting. As shown in Figure 8, although the rate constant k_c has about the same activation energy as k_a (or k_b), the activation energy of k_d is about four times larger. At room temperature, the magnitude of k_d is nearly a factor of 30 slower (3.1×10^{-1} sec^{-1} for k_c versus 1.0×10^{-2} sec^{-1} for k_d). Thus, if we take the k_c rate constant to be associated with the cis isomer, then k_d is probably associated with the reorientation of the trans form in the vertical direction. The large activation energy associated with the trans form is

probably due to its more extended configuration, hence experiencing a greater friction as the reorientation takes place.

Consider finally the effect of the film thickness. Rochon et al.[12] previously searched for the net maximum birefringence obtainable and have investigated the growth rates as a function of film thickness. The film thickness was emphasized because of their earlier conclusion about the time required for the chromophores to exhibit an anisotropy in the orientational distribution depending on the intensity of the writing beam. They have argued that, due to large laser intensity absorption by the azobenzene moiety, the intensity of the writing beam decreases rapidly as a it propagates through into the specimen. Hence, they expected to observe the molecular reorientation rates to depend on the thickness of the film. These authors have then presented a simulation to calculate the induced phase retardation. The phase retardation is proportional to Δn. The simulation based on their assumed model reproduces the thickness dependence hypothesis.

Shown in Figure 9 are a series of transmitted intensity curves obtained by using methyl red/polystyrene films of different thickness. The thickness of the film is obtained with a Matricon, an instrument for determining the refractive index and film thickness based on the waveguide principle. Over the sample thickness range studied, the transmitted birefringence signal increases with the thickness of the film. We have analyzed the growth and decay segments of the transmitted signal and found that both the growth and decay segments fit rather well to the bi-exponential functions given by Eqs.(1) and (2). As shown in Figure 10, the rate constants k_a, k_b, k_c, and k_d do not change with the sample thickness. The amplitude factor of the fast process A decreases with increasing film thickness where the reverse is found for B. These data are consistent with the intensity

dependence shown in Fig. 6, but are in contrast to the simulation result of Rochon et al. which show a significant decrease in the growth rate for thick films, which they have interpreted as due to a decrease in the intensity of the writing beam as it penetrates into the sample.

In summary, we have investigated the growth and decay processes of the optically induced birefringence in azo benzene functionalized polymer (DR19FPOZ) and contrasted the results with a DR1/PMMA guest -host system. In the functionalized polymer, if the birefringence is not erased by a circular-polarized light, the decay segment of the signal does not decay to the background within the time of experiment. Both cis and trans isomers are found to contribute to the birefringence signal. The shape of the growth and decay segments of the birefringence signal are reflected by the orientational distribution of the cis and trans isomers, despite the fact that the temporal dependence of each segment can be fit to a bi-exponential function. In contrast to the previously reported results in the literature, the rate constants associated with the bi-exponential function are found to be independent of the intensity of the writing laser, although the amplitudes of the exponentials in the growth segment are found depend on the laser intensity. Temperature dependent studies of the birefringence signal show that the slow process in the decay segment has a significantly greater activation energy than the fast process. This allows an assignment of the fast process to be associated with the reorientation of the cis isomer, and the slow one with the trans isomer. The film thickness dependence study of the birefringence signal has also yielded results consistent with the intensity data. The kinetic rate constants are independent of the film thickness.

These results can be understood because the photoinduced trans to cis or cis to trans isomerization process involves elctronic transitions associated with the breaking of a chemical bond (a π-π bond). Despite the rates of these isomerization processes strongly dependent on the laser power, the kinetics for the photoinduced isomerization are rather fast. In the slow time scale involving the birefringence signal measurement, only reorientational motions of the final products of the photoisomerization process are involved, and the writing laser power dependence should not be expected. The kinetics rate constants obtained as k_a and k_b in the growth segment and k_c and k_d in the decay segment are due to the slow reorientation process of the trans and cis isomers. These are intrinsic material constants and should be independent of the laser intensity or sample thickness, despite the fact that the amplitude factors associated with the growth segment may depend on the writing laser intensity as these are related to the amount of the isomers produced by the writing laser.

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Figure captions

Fig. 1: Chemical structure of DR19 functionalized polyoxazolidone (DR19FPOZ) polymer.

Fig. 2: Experimental setup for the measurement of the photoinduce orientation of azo compound. Various letters designate various optical and electronic components. M: mirror; S: shutter; P: polarizer; PR: polarization rotator; L: lenz; NF: neutral density filter; H: pinhole; F: filter set; PMT: photomultiplier tube; PC: personal computer.

Fig. 3: Typical growth and decay processes of photoinduced birefringence. Top is for a guest/host DR1 in PMMA polymer and bottom is for DR19FPOZ at room temperature. Pump beam is on at "A" and off at "B". Circular polarized light was introduced at "C".

Fig. 4: Temperature dependence of the photoinduced birefringence signal, temperature increases from top to bottom, following the numerical order given in the figure.

Fig. 5: Comparison of the growth (top) and the decay (bottom) of the photoinduced birefringence. Solid lines are the fitted curves.

Fig. 6: Writing power dependence of rate constants(top and middle) and amplitudes (bottom) of the growth and the decay of the photoinduced birefringence.

Fig. 7: Arrhenius plots of the relaxation rate constants of DR19FPOZ in the growth region. Open and closed circles are for k_a and k_b, respectively.

Fig. 8: Arrhenius plots of the relaxation rate constants for DR19FPOZ in the decay region. Open and closed circles are for k_d and k_c, respectively.

Fig. 9: Film thickness dependence of the photoinduced birefringence with 2 wt% methyl red in polystyrene.

Fig. 10: Rate constants derived from the growth (top) and the decay (bottom) segments of the photoinduced birefringence signal ploted versus the film thickness..

Fig 1.

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Writing Beam

Ar ion laser

M

S

P

PR

L

M

Reading Beam

He:Ne laser

M

PC

M

NF   L   P   Film

H P F

PMT

Fig 2

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Fig. 3

Fig 4

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Fig 5

Sarg et al.

$E_a = 6.6 \ (\pm 0.5)$ kcal/mol

k_a

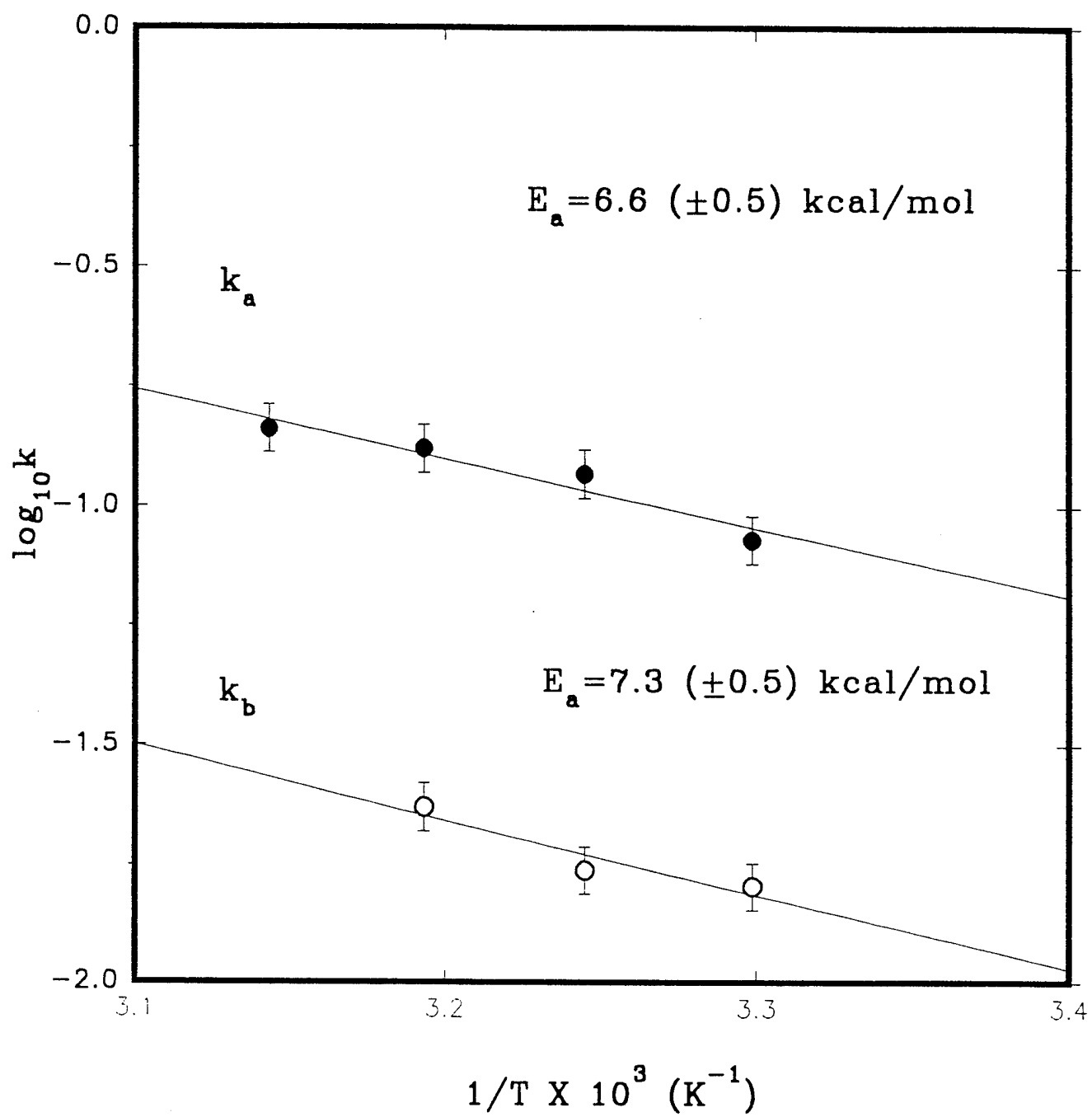$E_a = 7.3 \ (\pm 0.5)$ kcal/mol
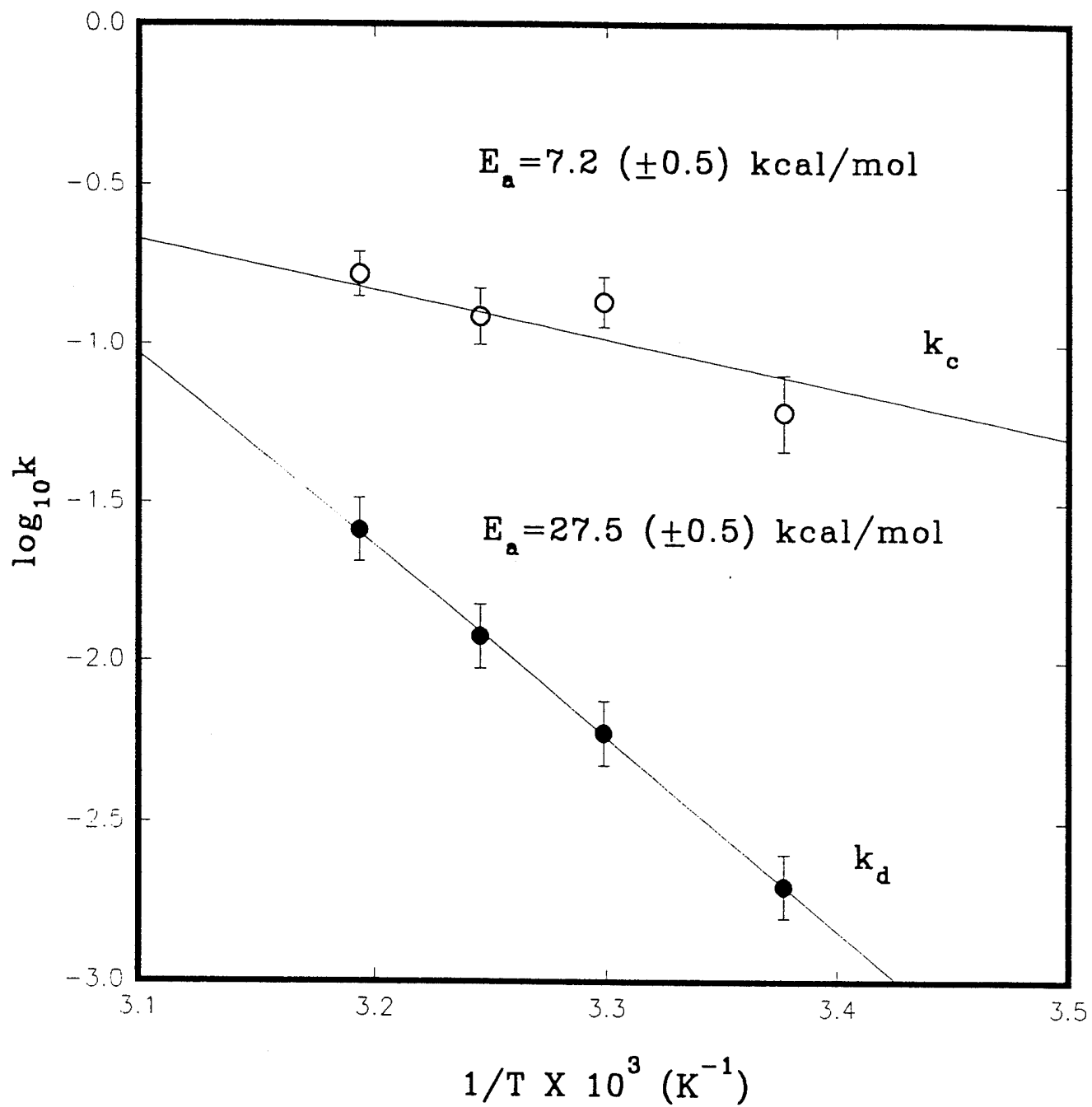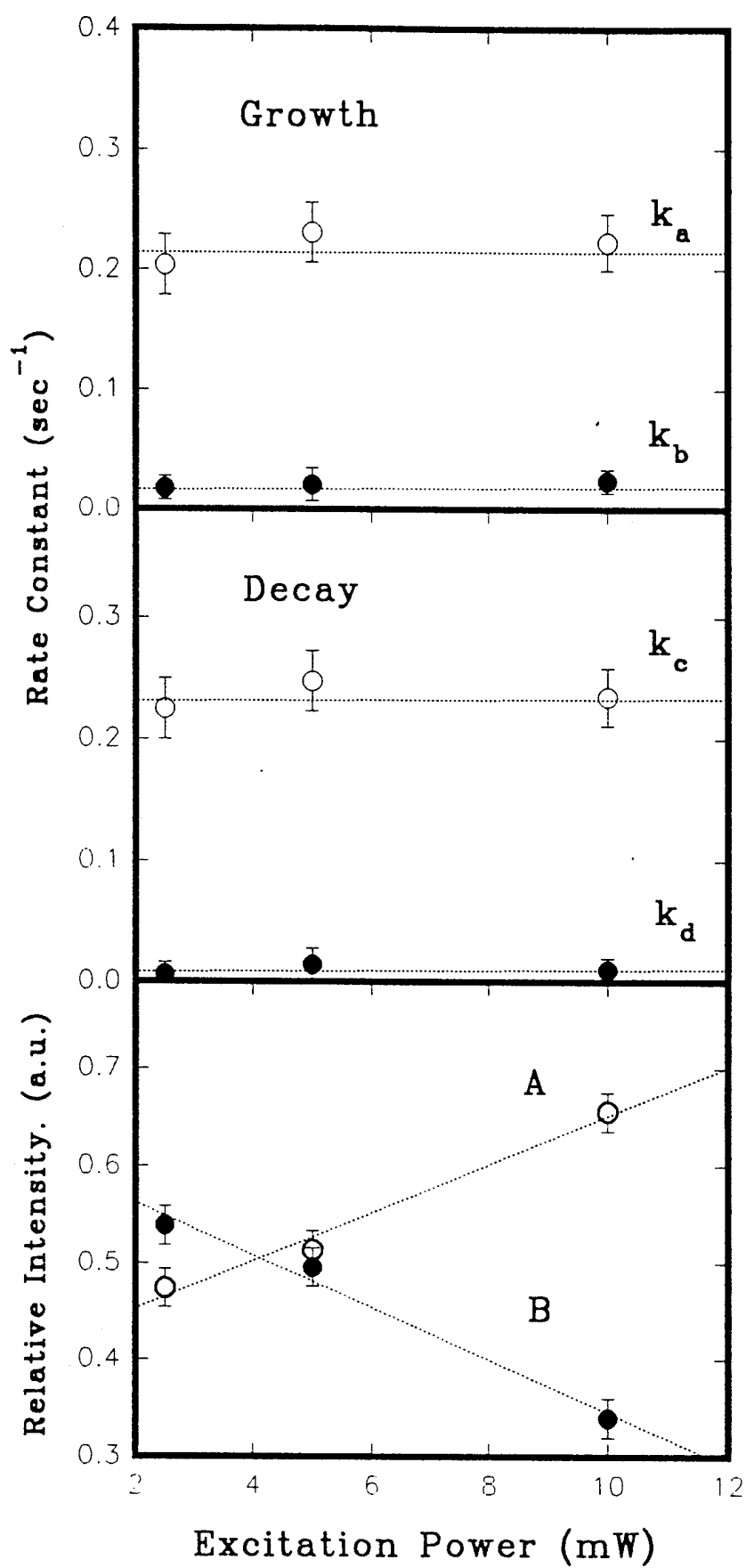
k_b

$\log_{10} k$

$1/T \ X \ 10^3 \ (K^{-1})$
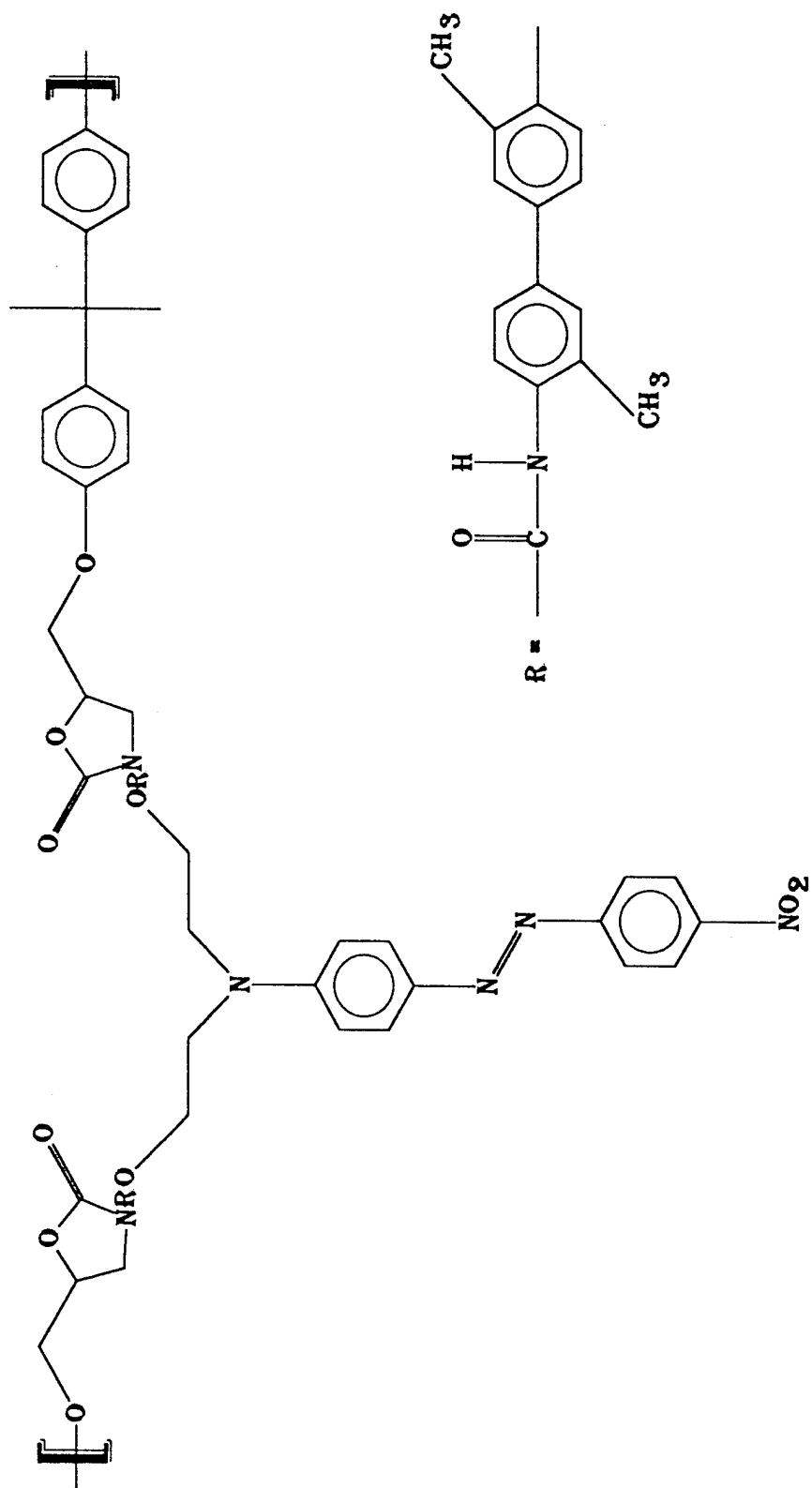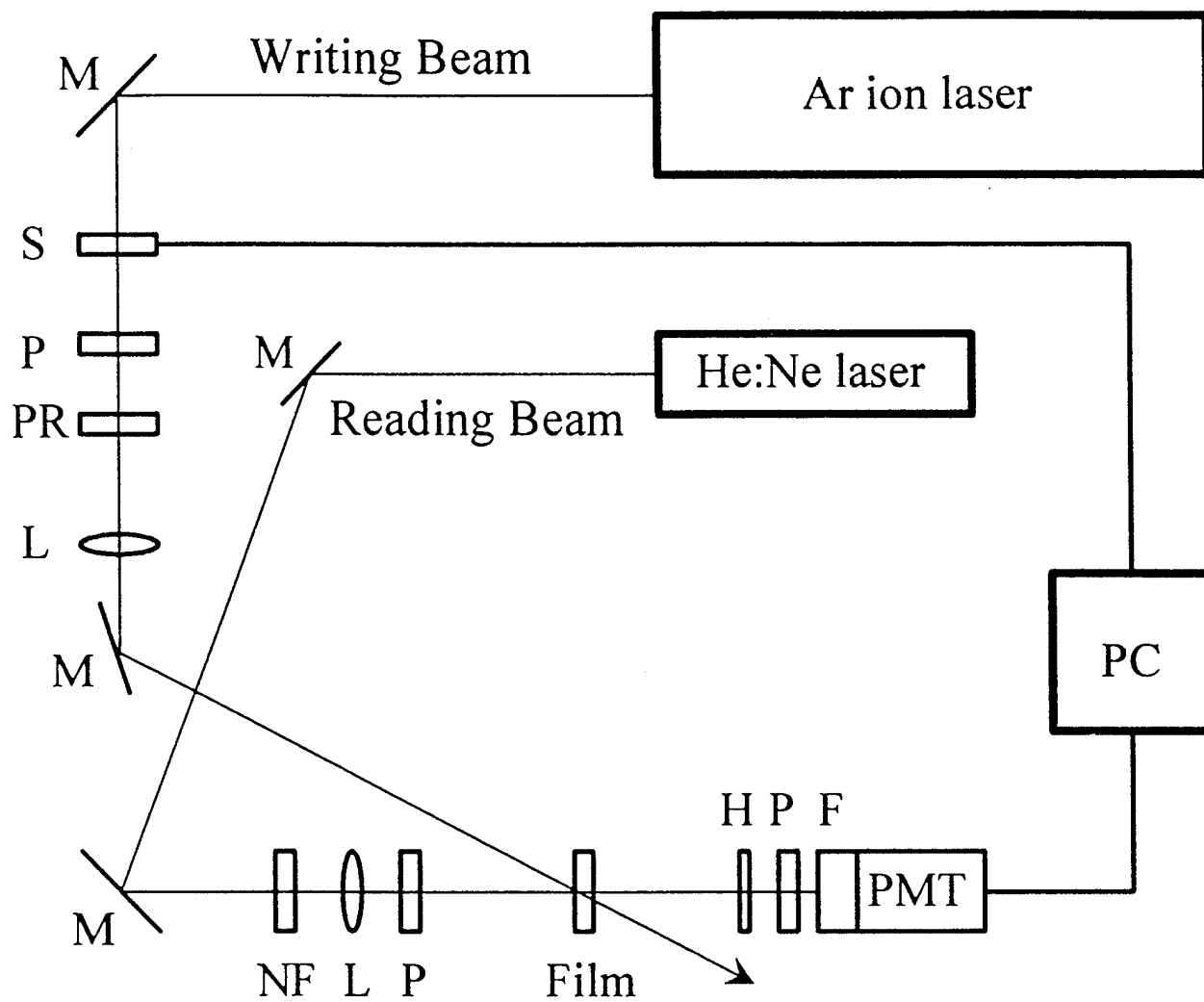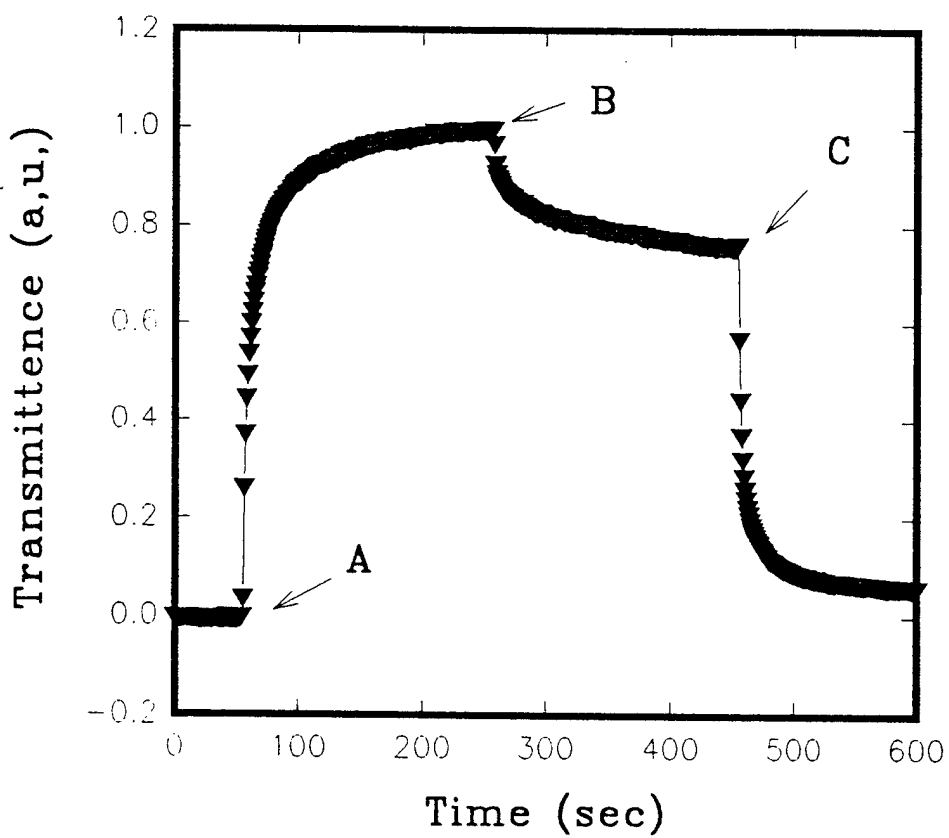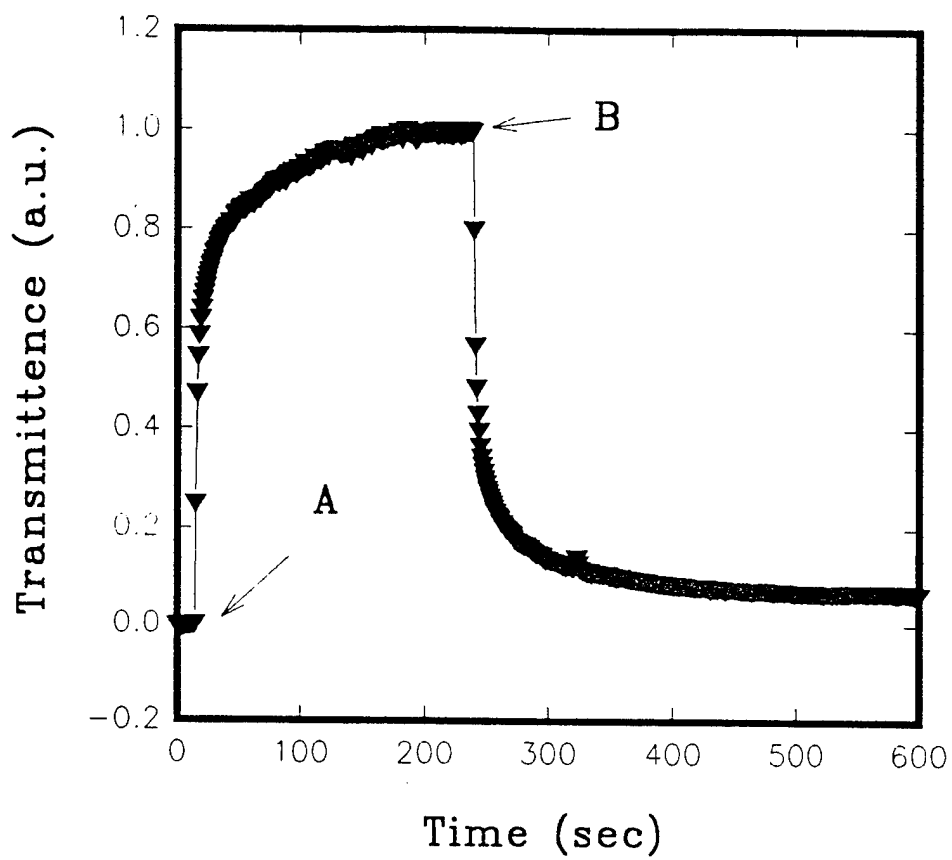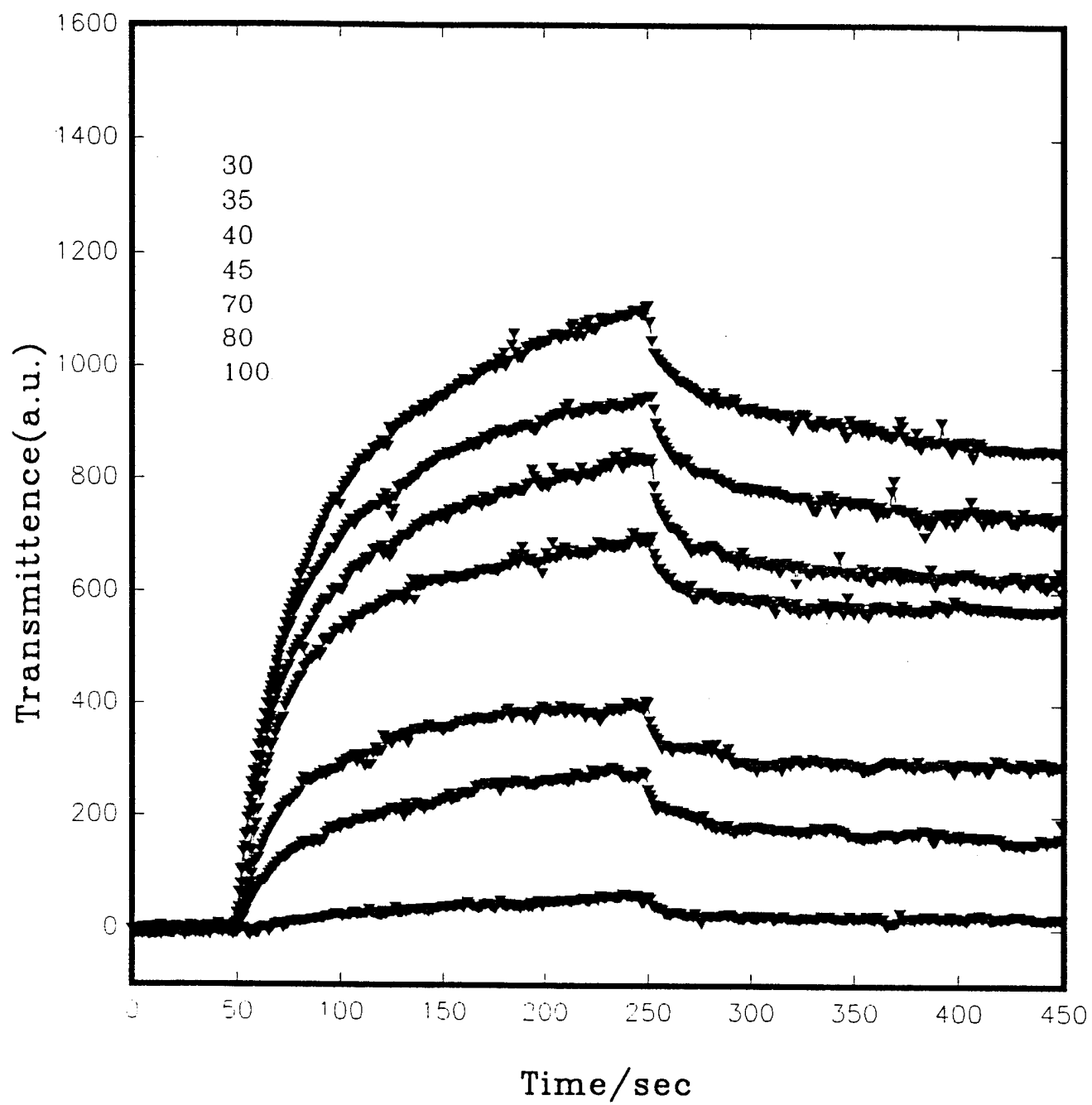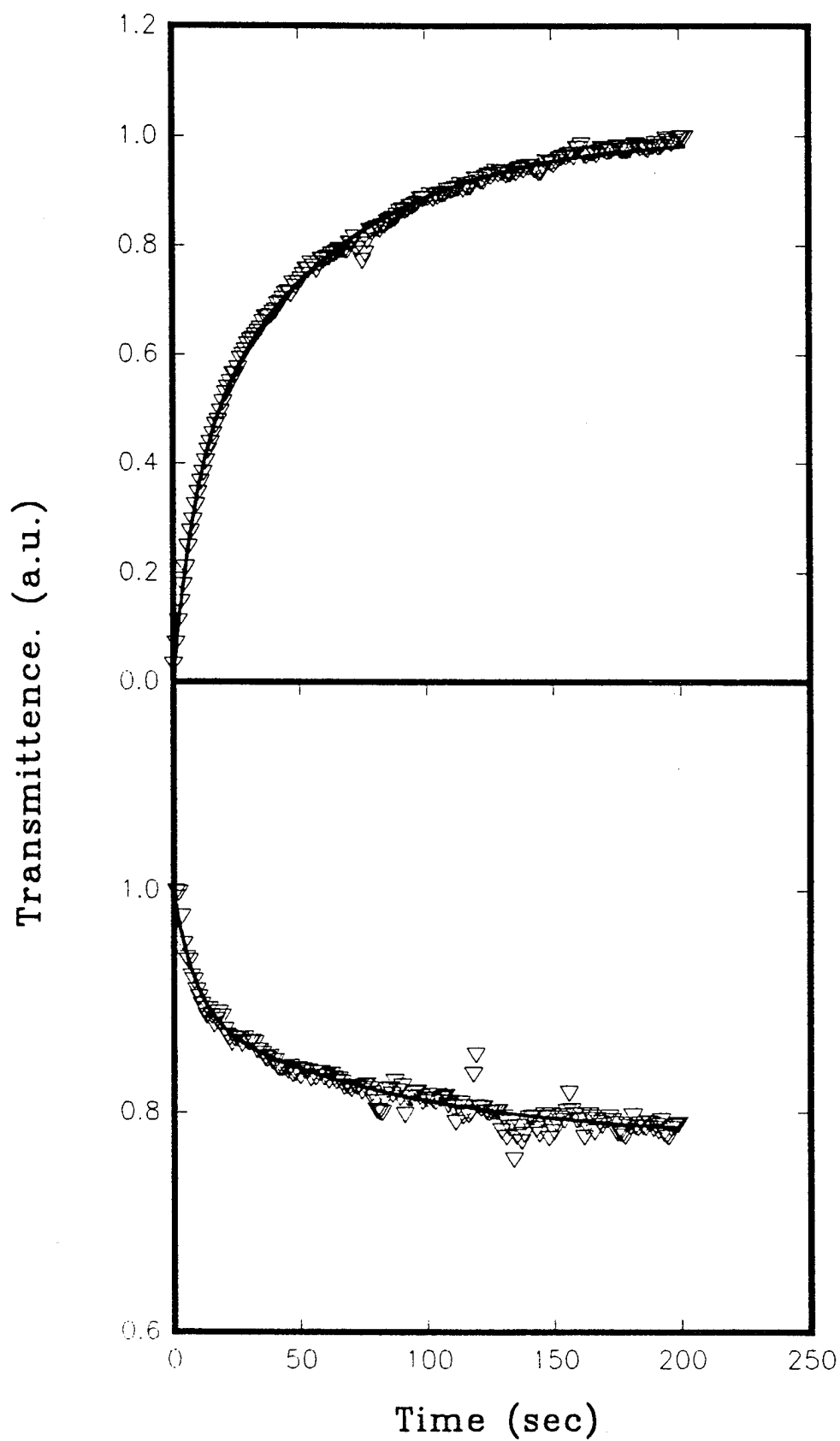
Fig 6

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Fig 7.
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Fig 8

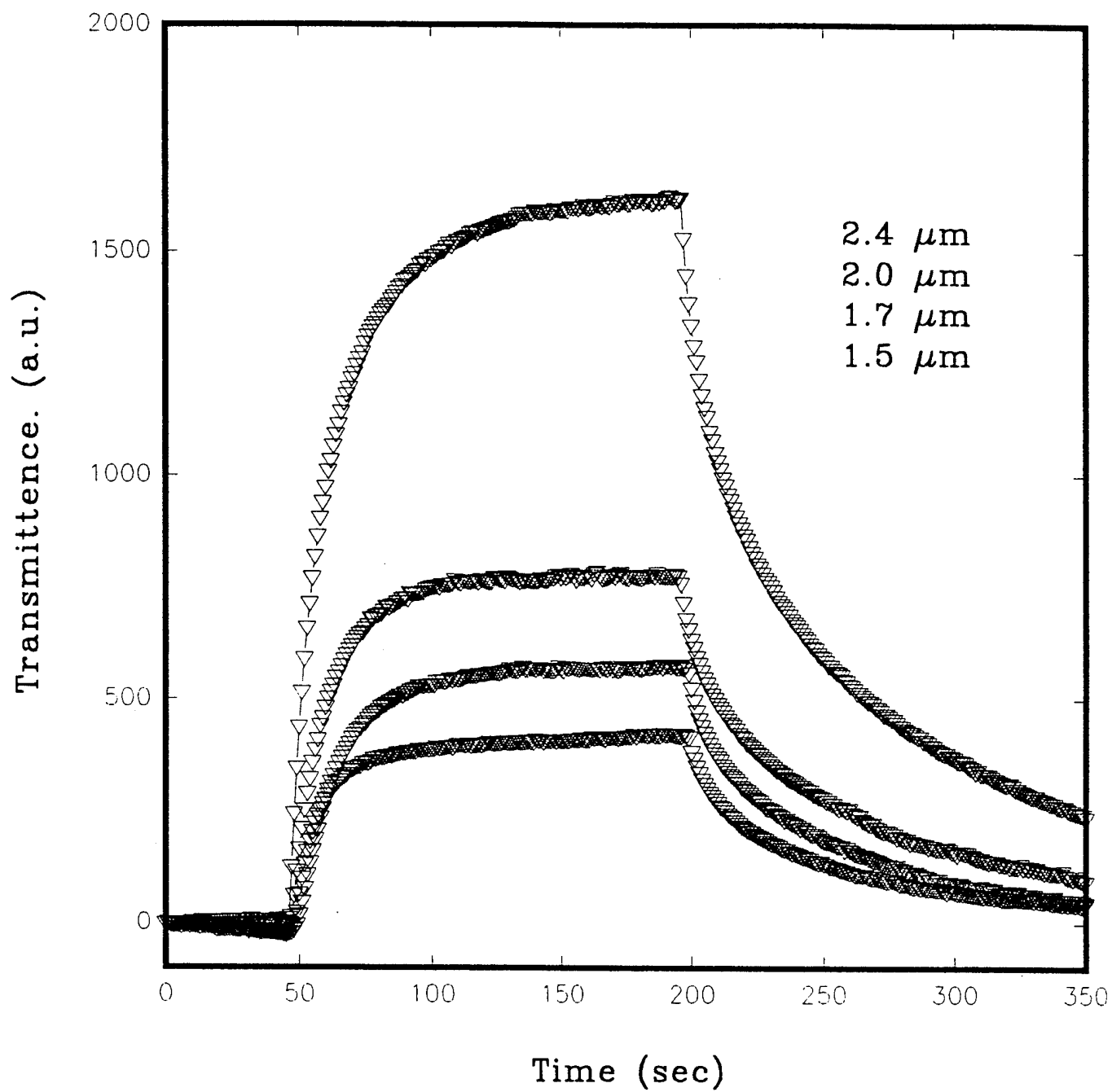Song et al.

Fig 9.

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Fig 10

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